Photoluminescence pressure coefficients of InAs/GaAs quantum dots

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Abstract

We have investigated the band-gap pressure coefficients of self-assembled InAs/GaAs quantum dots by calculating 17 systems with different quantum dot shape, size, and alloying profile using atomistic empirical pseudopotential method within the "strained linear combination of bulk bands" approach. Our results confirm the experimentally observed significant reductions of the band gap pressure coefficients from the bulk values. We show that the nonlinear pressure coefficients of the bulk InAs and GaAs are responsible for these reductions. We also find a rough universal pressure coefficient versus band gap relationship which agrees quantitatively with the experimental results. We find linear relationships between the percentage of electron wavefunction on the GaAs and the quantum dot band gaps and pressure coefficients. These linear relationships can be used to get the information of the electron wavefunctions.

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Self-assembled InAs quantum dots (QDs) grown on lattice-mismatched GaAs(100) substrates have been studied extensively in both experiment and theory in the past 15 years due to their potential applications and matured synthesise processes [1]. Depending on synthesise methods and conditions, the quantum dot can have different size, shape and alloy profile. A major task of the research is to study the dependence of the electronic structure on the size, shape and alloy profile. The electronic structure includes the electron wavefunctions and their eigen energies. While there are many experimental ways to probe the electron eigen energies and their confinement effects [e.g, photoluminescence (PL) for the exciton energy; the capacitance charging experiment for Coulomb interaction and the single particle levels [2]], it is much more difficult to experimentally measure the electronic wavefunctions. Magnetotunneling spectroscopy [3], low-temperature scanning tunneling spectroscopy [4], and near-field scanning optical microscopes [5] have been used to probe the electron wavefunctions, but they are not always successful, and the information about the electron wavefunctions remain extremely scarce. Thus any information about the electron wavefunctions will be extremely useful.

One recently popular experimental approach to study the electronic structure of a QD is to measure their pressure dependences of the PL energies. While the PL pressure coefficients (PC) for both bulk InAs and GaAs are close to 120 meV/GPa, it is found experimentally that the PL pressure coefficients for the quantum dots are usually much smaller and they can vary significantly from 60 meV/GPa to 100 meV/GPa [6, 7, 8, 9, 10, 11] depending on the samples. While Ma *et al.* attributed the main reason for the much smaller PC to the built-in strain in InAs dots under nonlinear elasticity theory [6], Mintairov *et al.* emphasized the nonuniform In distribution in QD [13]. Thus more quantitative analysis and understanding are needed here. It is also interesting to find whether the measured PC of a QD can be used to infer other properties of the system, e.g., of the electron wavefunctions.

In this letter, via accurate atomistic calculations for the electron wavefunctions for these quantum dots, we show that the nonlinear elasticity and the nonlinear band gap pressure dependence are responsible to the reduction of PC. One problem of embedded QD study is the lack of reliable experimental information for the QD size and shape. To overcome this, we have studied 17 different QD systems covering the possible experimental ranges of QD size and shape. What we find, surprisingly, is a universal relationship between the QD exciton energy (PL energy) and the pressure coefficients, which can be compared directly with the

experimental results. Our calculated PC/exciton energy relationship agrees excellently with the experimental measurements. Furthermore, we show that both the QD band gaps and their PC correlate linearly with the percentage of the electron wavefunctions on top of the GaAs materials. This is independent of the QD size, shape, and alloy profile. As a result, these linear relationships and the corresponding PL and PC experiments can be used to get the information of the electron wavefunctions.

We will use the empirical pseudopotential method (EPM) [14] to describe the single electron wavefunctions $\psi_i(\mathbf{r})$ of an InAs quantum dot embedded in a GaAs matrix:

$$(-\frac{1}{2}\nabla^2 + V(\mathbf{r}) + V_{NL})\psi_i(\mathbf{r}) = E_i\psi_i(\mathbf{r}), \tag{1}$$

here the total potential $V(\mathbf{r})$ of the system is a direct sum of the screened atomic empirical pseudopotentals $\nu_\alpha(r)$ of the constituent atoms (type α), and V_{NL} is the nonlocal potential describing the spin-orbit interaction. The EPM approach has been used to study InAs/GaAs systems extensively, including quantum dots and alloys. Its results agree well with experiments [15]. To study the various quantum dots in our problem, we need computational supercells containing up to one million atoms. The wavefunctions in Eq(1) is expanded by planewave basis. In average, each atom will have ~ 50 planewave basis functions. Thus the Eq(1) corresponds to a ~ 50 million degree of freedom problem. To solve Eq(1), we have used the strained linear combination of bulk band (SLCBB) method [16]. In this method, the wavefunction $\psi_i(\mathbf{r})$ is expanded by bulk Bloch states (which is in turn expanded by planewaves). Because the bulk Bloch states are good physical basis functions for the quantum dot states, we can truncate this basis set (down to 10,000) using physical intuition without introducing significant errors. The errors caused by the SLCBB method are around 10 meV near the band gap compared with the exact solution of Eq(1) [17]. As a result, this is a much more accurate method compared to other traditional approaches like the k.p method, where a few hundred meV error is possible [17].

To study the pressure effects on the electronic wavefunction, we first need to study the lattice relaxation under the pressure. We have used the Keating's valence force field (VFF) [18, 19] to described the atomic relaxation. In order to describe accurately the bulk modulates and their high order pressure dependence, we have included bond-stretching, bond-bending, and bond-angle coupling interactions and high order bond-stretching terms [15]. Table I lists the VFF bulk modulates and their pressure dependence. They agree well with

the experiments. To be able to describe accurately the nonlinear lattice relaxation is important because there is a $\sim 7.2\%$ lattice mismatch between bulk InAs and GaAs. For a quantum dot system, InAs is under compressive stress and GaAs is under tensile stress. They will behave differently under additional external pressure because of the nonlinear lattice relaxation.

After the atomic relaxation is described accurately by the VFF model, the pressure dependence of the bulk band structures for GaAs and InAs is described by the EPM Hamiltonian. Here, an explicit local strain dependence of $\nu_\alpha(r)$ is used to describe accurately the deformation potentials of the band energies [15]. Thus the fitting of $\nu_\alpha(r)$ not only provide an accurate band structure at zero pressure, it also provides accurate high order pressure dependence of the band energies. Fig.1 shows the calculated band energy pressure dependence for bulk InAs and GaAs. The calculated band gap pressure coefficients for InAs and GaAs are 117 and 103 meV/GPa respectively, they agree well with the experimental values of 114 and 106(4) meV/GPa [20].

We next use the above VFF and EPM Hamiltonians to calculate various embedded quantum dots under different pressures. A large variety of QD shapes have been reported and studied for the InAs/GaAs system by various groups, for example pyramidal quantum dot (PQD) with side facets oriented along {101}, {113}, or {105} [21] or truncated pyramidal quantum dot (TPQD) [22, 23]. Inside the QD, various In/Ga profiles have been speculated, for example an inverted-triangle shape In-rich core [23] or a growth direction linearly increasing In concentration [22]. To cover the whole spectrum of possible shapes and alloy profiles, we have used three sets of QDs: pure pyramidal QDs with {101}, or {113}, or {105} facets; pure truncated pyramidal QDs with different height/base ratios; and linearly increasing In concentration alloy profile QDs. Besides the shapes and alloy profiles, different sizes of the same shape QD are used. In total we have calculated 17 different quantum dots, their sizes, shapes and alloy profiles are described in Table II.

The above described InAs quantum dots are embedded in a pure GaAs matrix. A supercell box is used to contain the quantum dot. A periodic boundary condition is used for the supercell box. To remove the possible dot-dot electronic and elastic interactions, sufficient GaAs barrier is used. As a result, a supercell can contain upto one million atoms. The atomic positions within the supercell are then relaxed by minimizing the strain energy of the VFF Hamiltonian. To create a pressure, the overall size of the supercell is changed, and

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the pressure is calculated from the local GaAs strains away from the quantum dot. After the atomic positions are relaxed, the electron and hole eigenstates and eigen energies of Eq(1) are solved using the SLCBB method.

We typically calculate 5 pressure values from 0 to 2 GPa for each quantum dot. Using these five points, the band gap of the quantum dot is fitted as $E_g(P) = E_g(0) + a_1 P + a_2 P^2$. Then the linear pressure coefficients (PC) of the band gap is read out from a_1. In consistent with the experiment, we find this PC is in the range of 60-110 meV/GPa, much smaller than the bulk InAs and GaAs PC. We then plot all the calculated PC as a function of the QD zero pressure exciton energy $E_0(0)$ (which is the band gap minus the electron hole interaction),the result is shown in Fig.2. Surprisingly, despite all the different shapes and sizes for the 17 QDs we studied, we find a rough universal linear relationship between the PC and the exciton energy. This provides a convenient way to compare with the experiment, without the need to know the QD size and shape which are not available from the experiment. The theory and experiment comparison is shown in Fig.2. The agreement is excellent considering all the possible uncertainties involved. We see that, indeed, the QD pressure coefficients are much smaller than the bulk values of both InAs and GaAs, and they decrease with the exciton energy.

To understand the variation of the PC, and its dependence on the QD, we can perform a simple analysis. We will concentrate on the conduction band minimum (CBM) state since most of the band gap pressure coefficient comes from the conduction band [24]. For a simple approximation, we can express the energy E_{CBM} of the CBM eigenstate $\psi_{CBM}(\mathbf{r})$ as a sum of an effective mass like potential energy and a kinetic energy E_k, and the potential energy can be approximated by a weighted sum of the local conduction band energy:

$$E_{CBM} \approx \int |\psi_{CBM}(\mathbf{r})|^2 E_c(\mathbf{r}) d^3 r + E_k, \qquad (2)$$

here the $E_c(\mathbf{r})$ is the bulk conduction band energy for the given local strain at $\mathbf{r}$ and the local constituent material (either GaAs or InAs). Note that, in practice, the space integral of Eq(2) is replaced by a sum over the atom $\sum_{at} W_{at} E_c(at)$, where the local strain for an atom is calculated from the atom's nearest neighbor atomic positions, and W_{at} denotes the weight of $|\psi_{CBM}(\mathbf{r})|^2$ at that atom "at". We have plotted E_{CBM} as a function of $\sum_{at} W_{at} E_c(at)$ in Fig.3(a). We see that all the calculated QDs fall into a nice curve. The difference between this curve and the dashed line (the potential energy line) is the kinetic energy E_k.

Now, we analysis the pressure coefficients of E_{CBM} using Eq(2). If we ignore the pressure dependences of the kinetic energy and the weight function W_{at}, we can have an approximated relationship:

$$E'_{CBM} \approx \int |\psi_{CBM}(\mathbf{r})|^2 E'_c(\mathbf{r})d^3r, \tag{3}$$

here the prime indicate the derivation with pressure. Despite all the approximations, the left and right hand side of Eq(3) do form a nice linear relationship, as shown in Fig.3(b). The slope of the line in Fig.3(b) is not 1, but 1.25, indicating the right hand side of Eq(3) account only for about 80% of the left hand side. This situation can be compared with the case of free standing colloidal quantum dots [25], where the change of PC in a QD can be traced back completely from their bulk origin. Our current embedded QD is much more complicated due to the internal strain effects between InAs and GaAs, we find such accurate analysis is impossible here.

Despite of not accounting 100% of the left hand side in Eq(3), the physical meaning of the right hand side of Eq(3) is clear and useful [especially when it is written as $E'_{CBM} \approx \sum_{at} W_{at}E'_c(at)$]: the PC of the quantum dot state is a wavefunction weighted sum of the local PC at all the atoms. The $E'_c(at)$ depends on the local strain of this atom as illustrated in Fig.1. This can be used to understand why the QD PC is in general less than the bulk InAs and GaAs results. Because InAs in the QD is always under compressive strain, due to the nonlinear PC as shown in Fig.1, the E'_c in the InAs region is significantly smaller than its bulk value of 130 meV/GPa. On the other hand, GaAs is under tensile strain, which will increase E'_c. However, because the magnitude of the GaAs strain is in general smaller than the InAs strain, and because most wavefunction is localized in the InAs region, the averaged PC is then smaller than the bulk InAs and GaAs PCs. Thus we see that the nonlinear bulk PC is responsible for the reduction of QD PC compared to bulk values, in consistent with the explanation provided by Ma et al [6].

Guided by Eqs(2),(3), we now try to find some simple relationships between the experimentally easily observable quantities (band gap and pressure coefficients) and the wavefunction properties. In Eq(3), if we represent $E'_c(at)$ by just two values, one for InAs, one for GaAs, then E'_{CBM} of Eq(3) becomes an linear function of $x = \sum_{at\in GaAs} W_{at} / \sum_{at\in all} W_{at}$ (i.e, the percentage of the wavefunction on GaAs). This hypothesis is tested in Fig.4(a), where we have plotted the pressure coefficients of the exciton energy (not just the CBM energy), so the connection with experiment is more straightforward. We see that E'_0 and

x form a very nice straight line. This can be very useful, since a measured E_0' value will give us the x, which is a property of the wavefunction that cannot be measured easily by other means. The same relationship can be plotted between the exciton energy itself E_0 and the x, as in Fig.4(b). They also form a rough linear relationship although with larger scatters. The linear relationships in Fig.4(a) and (b), in turn, explain why we have a rough universal relationship between E_0' and E_0 in Fig.2. This is because both E_0' and E_0 are linearly correlated with x.

In summary, using accurate and reliable empirical pseudopotential methods and the SLCBB calculations, we have studied InAs/GaAs quantum dot PL pressure coefficients. We investigated 17 different quantum dots covering the ranges of experimental QD size, shape and alloy profile. We found a universal PC and exciton energy relationship, which agrees excellently with the experimental results. We also find linear relationships between the wavefunction percentage on GaAs and the PL pressure coefficient and PL energy. These linear relationships can be used to probe the properties of the electron wavefunctions.

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TABLE I: The VFF bulk modulates and their first and second order pressure coefficients. The bulk modulates are in the unit of $10 GPa$, the dB/dP has a unit 1, and d^2B/dP^2 is in the unit of GPa^{-1}.

Property	GaAs		InAs	
	Fitted	Expt.[a]	Fitted	Expt.[a]
C_{11}	12.11	12.11(4)	8.328	8.329
C_{12}	5.50	5.48(17)	4.553	4.526
C_{44}	6.04	6.04(2)	3.803	3.959
B	7.70	7.54	5.811	5.794
dB/dP	5.01	4.49	5.329	4.787
d^2B/dP^2	-0.111	—	-0.144	—

[a]Reference [20]

TABLE II: The 17 calculated quantum dots

| Pure InAs pyramidal quantum dots (PQDs)							
	1	2	3	4	5	6	7
facet	{101}	{101}	{113}	{113}	{105}	{105}	{105}
base size(nm)	6	11.3	6	11.3	11.3	15	20
Pure InAs truncated pyramidal quantum dots (TPQDs)							
	8	9	10	11	12	13	14	15
facet	{101}	{101}	{101}	{101}	{101}	{101}	{101}	{101}
base size(nm)	6	6	6	11.3	11.3	11.3	11.3	11.3
height/base	2/3	1/2	1/4	2/3	1/2	1/4	1/5	1/10
Alloy pyramidal quantum dots							
	16	17
facet	{101}	{101}
base size(nm)	11.3	11.3
alloy profile	bottom 40%Ga, tip 0%Ga	bottom 50%Ga, tip 0%Ga
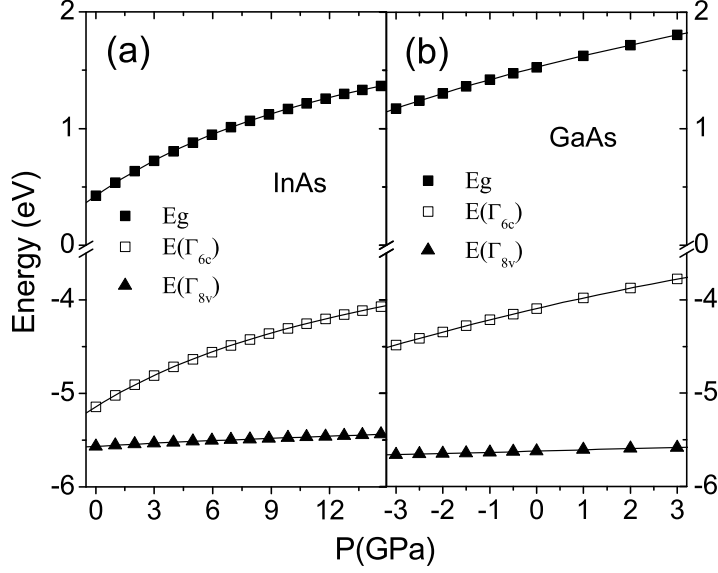
FIG. 1: The band-edge energies ($E(\Gamma_{6c})$, and $E(\Gamma_{8v})$) of (a) bulk InAs and (b) GaAs and their direct band gap $E_g(\Gamma_{8v} - \Gamma_{6c})$ under hydrostatic pressure.
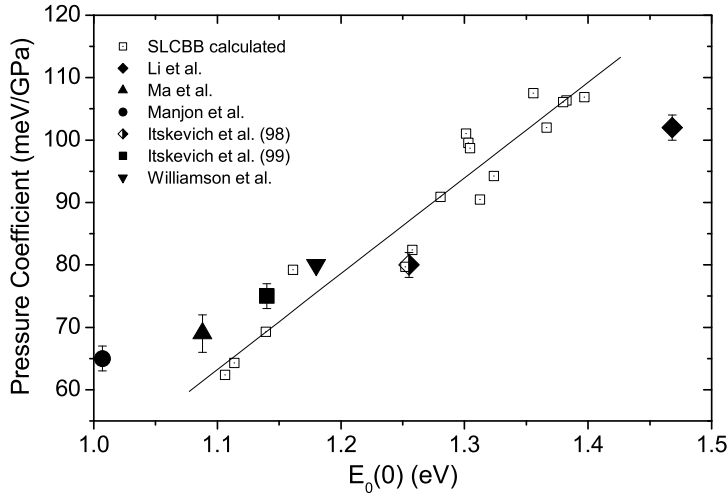

FIG. 2: The PL pressure coefficient (E'_0) versus $E_0(0)$ (PL energy) and comparison with experiments. The $E_0(0)$ is the zero pressure exciton energy which equals the band gap minus the electron hole Coulomb interaction. The experimental results are: Li *et al.* [11], Ma *et al.* [6], Manjon *et al.* [7], and Itskevich *et al.* [9, 10]. We also included one previously calculated result from Williamson *et al.* [12].
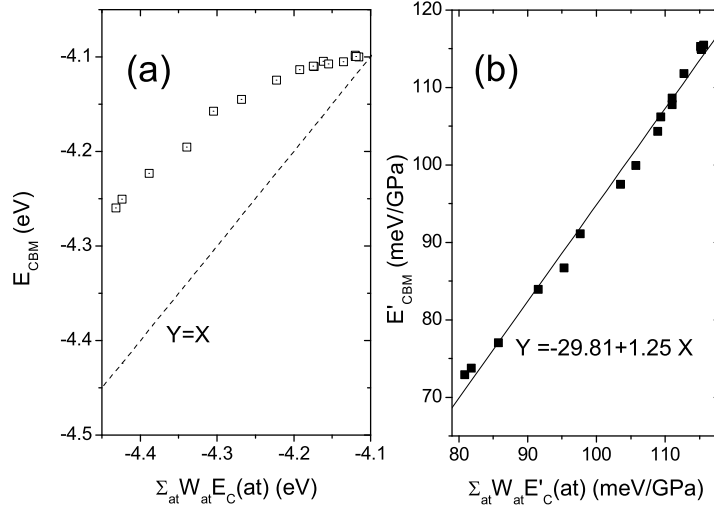
FIG. 3: (a) The E_{CBM} as a function of $\sum_{at} W_{at} E_c(at)$; (b)The E'_{CBM} as a function of $\sum_{at} W_{at} E'_c(at)$.
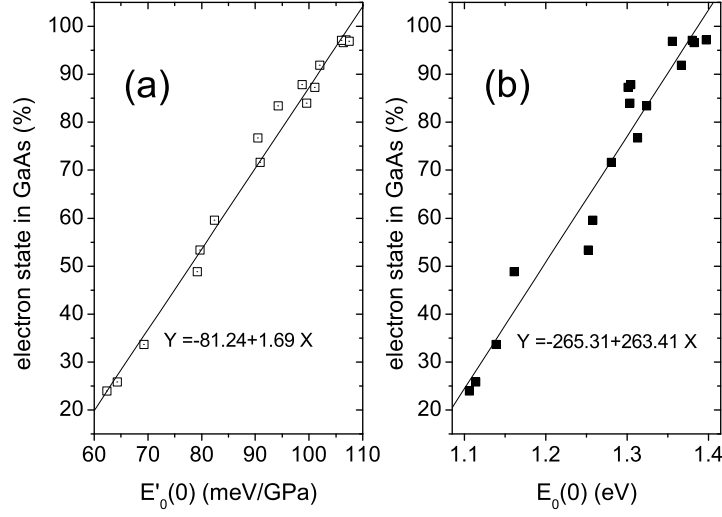

FIG. 4: (a)The relationship between $E'_0(0)$ and x (the percentage of the electron state in GaAs); (b) The relationship between $E_0(0)$ and x.